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# SCIENTIFIC PAPERS

OF THE

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No. 467

[Part of Vol. 18]

## SPECIFIC VOLUME OF SATURATED AMMONIA VAPOR

BY

C. S. CRAGOE, Physicist

E. C. McKELVY, Chemist

G. F. O'CONNOR, Laboratory Assistant

*Bureau of Standards*

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MARCH 17, 1923.



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THE HISTORY OF THE  
CITY OF BOSTON  
FROM 1630 TO 1800

BY  
JOHN H. COLEMAN



# SPECIFIC VOLUME OF SATURATED AMMONIA VAPOR.

By C. S. Cragoe, E. C. McKelvy, and G. F. O'Connor.

## ABSTRACT.

Measurements of the specific volume of saturated ammonia vapor were made in the temperature interval  $-50$  to  $+50^{\circ}$  C. by two methods. The first method involved the direct determination of the mass of the vapor contained in a known volume using three calibrated glass picnometers. The effect of adsorption of ammonia on the walls of the picnometer was studied and found to be no greater than the inherent inaccuracies of that method. In the second method the refractive index  $n$  of the vapor was measured, using a Fizeau-Pulfrich interferometer, and the specific volume  $u'$  was calculated from the Gladstone and Dale relation  $u'(n-1)=\text{constant}$ .

Values of the specific volume computed by the Clapeyron equation from other measured thermodynamic properties of ammonia were found to represent closely the mean of the results found by the two methods. The final results are expressed by means of an empirical equation which forms the basis of the appended tables in metric and English units.

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## I. INTRODUCTION.

The specific volume, or the volume occupied by unit mass, of a vapor under saturation conditions is a quantity difficult to determine with high accuracy. This is particularly true in the case of ammonia vapor at low temperatures (below  $0^{\circ}$  C.) where the mass to be measured is small. It is perhaps for this reason that experimenters have confined themselves in the past to measurements above  $0^{\circ}$  C. and have been content with calculated values for lower temperatures.

Direct measurements of the specific volume of ammonia involving a determination at various temperatures of the mass of saturated vapor contained in a known volume were undertaken at the Bureau of Standards several years ago. The precision of these measurements below  $0^{\circ}$  C. proved to be less than was hoped, and an optical method, in which the specific volume of the vapor was calculated from its measured index of refraction, was also employed. This work was interrupted during the war and the subsequent death of one of the authors <sup>1</sup> and the absence of the other authors from the bureau has delayed the publication of the results.

The present paper is the last of a series of papers <sup>2</sup> on the determination of the thermodynamic properties of ammonia under saturation conditions. The latent heat of vaporization, the specific volume of the liquid, and the vapor pressure having been determined with high precision, it is possible to compute the specific volume of the saturated vapor by means of the Clapeyron equation. The values computed in this manner are compared with the results obtained by the two methods to be described in this paper.

## II. PREVIOUS MEASUREMENTS.

The results of previous measurements and also computed values of specific volume are compared with the final results of the present work in Figure 1. Four of the curves represent the deviations of values computed by Wobsa,<sup>3</sup> Holst,<sup>4</sup> Goodenough and Mosher,<sup>5</sup>

<sup>1</sup> The untimely death of Mr. McKelvy resulted from an accident in the laboratory while working on the properties of ammonia.

<sup>2</sup> Specific Heat of Liquid Ammonia, B. S. Bulletin, 14, p. 397; 1917 (Scientific Paper No. 313); Jour. Amer. Chem. Soc., 40, p. 1; 1918; Jour. Amer. Soc. Refrig. Eng., 4, p. 134; 1917. Latent Heat of Vaporization of Ammonia, B. S. Bulletin, 14, p. 439; 1917 (Scientific Paper No. 315); Jour. Amer. Chem. Soc., 40, p. 14; 1918; Jour. Amer. Soc. Refrig. Eng., 4, p. 172; 1917. Vapor Pressure of Ammonia, B. S. Scientific Papers, 16, p. 1, 1920 (Scientific Paper No. 369); Jour. Amer. Chem. Soc., 42, p. 206; 1920; Jour. Amer. Soc. Refrig. Eng., 6, p. 307; 1920. Specific Volume of Liquid Ammonia, B. S. Scientific Papers, 17, p. 287; 1921 (Scientific Paper No. 420); Jour. Amer. Soc. Refrig. Eng., 7, p. 113; 1920.

<sup>3</sup> Zeitschrift für die gesamte Kälte-Industrie, 15, p. 11; 1908.

<sup>4</sup> Bull. Assoc. International du Froid, 6, No. 51; 1915.

<sup>5</sup> Univ. of Ill., Exp. Station, Bulletin, No. 66; 1913.



and Keyes and Brownlee<sup>6</sup> by means of their respective equations of state of ammonia. The dotted curves show the trend of the results obtained by the two methods described in this paper.

The first measurements of the specific volume of saturated ammonia vapor were made by Dieterici and Drewes.<sup>7</sup> Measurements in the temperature range 0 to +105° C. were made by Drewes, and measurements between 0 and +50° C. were repeated by Dieterici with some improvements in the apparatus. The results of the later measurements were published in conjunction

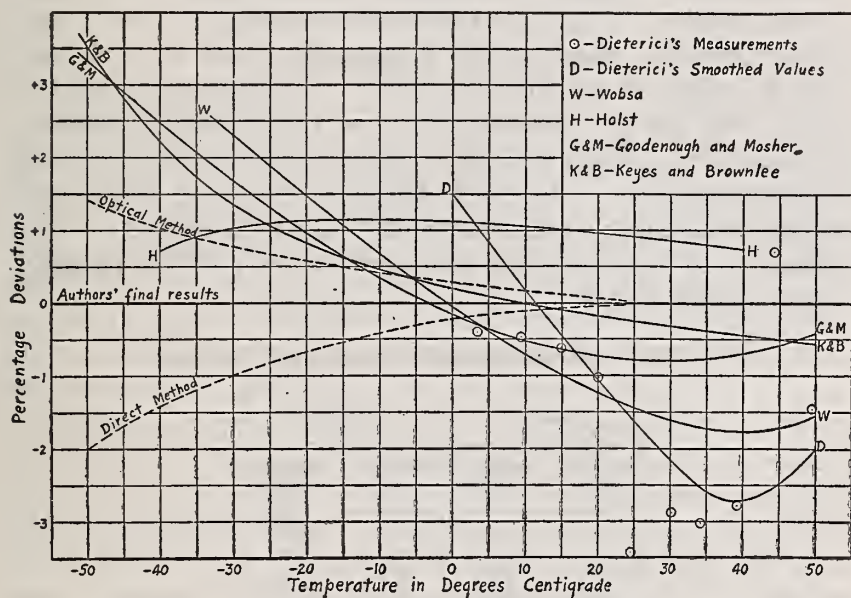


FIG. 1.—Percentage deviation of previous measurements and computed values of specific volume from the authors' final results.

with those of the earlier set between 50 and 105° C., Dieterici deeming their reliability to be such that repetition was unnecessary.

The method employed by these experimenters was to fill two glass vessels of different total volumes with equal masses of ammonia. Both vessels were immersed simultaneously in a thermo-regulated bath and observations were taken of the volume of the liquid in each vessel. The ratios of the specific volumes at the various observed temperatures were computed by the expression

$$R = \frac{u'}{u} = \frac{(V_2 - v_2) - (V_1 - v_1)}{v_1 - v_2}$$

<sup>6</sup> Thermodynamic Properties of Ammonia, John Wiley & Sons; 1916.

<sup>7</sup> Zeitschrift für die gesamte Kälte-Industrie, 11, p. 21; 1904.

where  $V$  represents the total volume of the vessel,  $v$  the observed volume of liquid, and the subscripts refer to vessels one and two. With these values of  $R$  the specific volume of the liquid was obtained from the measurements with the smaller vessel by the relation

$$u = \frac{v}{M} + \frac{V-v}{MR}$$

and finally  $u'$  from  $Ru = u'$ .

The design of Dieterici's picnometers was not such as to admit of high precision. The vapor bulbs had a capacity of 10 cm.<sup>3</sup>, containing, therefore, about 30 mg of ammonia vapor at 0° C. and about five times that amount at 50° C. The accuracy claimed is about a half per cent, although some of the individual observations near 50° C. depart from any smooth curve that can be drawn by about 2 per cent. The results are given in Table 1, and a comparison with the present measurements is shown in Figure 1. The full-line curve represents the smoothed values used by Dieterici in his ammonia tables.

TABLE 1.—Measurements by Dieterici and Drewes.

Dieterici.		Drewes.	
Tempera- ture.	Specific volume.	Tempera- ture.	Specific volume.
° C.	cm <sup>3</sup> /g	° C.	cm <sup>3</sup> /g
3.4	257.2	55.4	52.8
9.5	208.2	60.4	48.1
15.0	173.9	60.9	47.2
20.1	147.5	62.8	45.4
24.65	125.2	71.1	37.22
30.3	106.6	79.8	30.0
34.3	93.8	81.2	29.92
39.3	82.5	87.2	26.23
44.4	74.3	92.6	23.10
49.6	63.2	98.1	20.11
		102.1	17.88
		105.6	16.11

Berthoud<sup>8</sup> measured the specific volume of the saturated liquid and vapor of ammonia at high temperatures for the purpose of determining the critical volume. Two calibrated glass tubes of different volumes were immersed in the vapors of various substances boiling under a constant pressure, and the volumes of the liquid and vapor were observed in each tube. The temperatures in each experiment were obtained from the vapor-pressure curve of the particular substance employed. No details are given

<sup>8</sup> Helvetica Chimica Acta, 1, p. 84; 1918.

which permit an estimate of the precision attained. The results obtained may be found in Table 2.

TABLE 2.—Measurements by Berthoud.

Tempera- ture.	Specific volume.	Tempera- ture.	Specific volume.
° C.	cm <sup>3</sup> /g	° C.	cm <sup>3</sup> /g
0.00	294.0	121.30	9.77
45.00	66.7	123.20	9.22
78.70	31.06	125.45	8.20
98.75	18.76	129.60	6.63
109.25	14.47	(132.30)	<sup>1</sup> (4.234)
116.40	11.45		

<sup>1</sup> Critical value obtained by extrapolation.

### III. DIRECT METHOD.

The method employed by Dieterici appeared simple and offered the advantage of permitting direct measurements of both the mass and volume of the vapor under saturation conditions. For the present investigation a modification of this method was adopted and glass containers of suitable capacity were designed to yield an accuracy of about 1 part in 1,000. Several difficulties arose in carrying out the measurements which tended to reduce this accuracy very considerably. These difficulties are discussed in detail in section 4.

The method consists, essentially, in observing at various temperatures the volumes of the liquid and vapor phases in equilibrium in a closed vessel. Assuming that the two phases are present and in equilibrium—that is, saturated—and that the walls of the vapor space are dry, then at any given temperature the total mass of ammonia  $M$  in any closed vessel is given by the equation

$$M = \frac{v}{u} + \frac{V-v}{u'} \quad (1)$$

where  $u$  and  $u'$  represent the specific volumes of the liquid and vapor, respectively,  $V$  the total volume of the vessel, and  $v$  the volume of the liquid. The specific volume of the vapor is given by

$$u' = \frac{V-v}{M - \frac{v}{u}} \quad (2)$$

in which  $M$ ,  $V$  and  $v$  are the measured quantities. In order to evaluate the correction for the mass of the liquid  $\frac{v}{u}$  a separate determination of the specific volume of the liquid <sup>9</sup>  $u$  was made.

<sup>9</sup> B. S. Scientific Papers, 17, p. 287; 1921 (Scientific Paper No. 420); A. S. R. E. Journal, 7, p. 113; 1920.



## 1. DESCRIPTION OF APPARATUS.

*Picnometers.*—The vessels, here called picnometers, were made from soda glass and annealed by E. O. Sperling of this bureau. The inside diameter of the capillary tubes was about 2 mm and the wall thickness about 3 mm. Scales were etched upon these capillaries and also upon the upper tubes by ruling divisions at intervals of 1.5 mm with a dividing engine.

Three picnometers, designated D, E, F, of different total volumes were used within the temperature range covered experimentally according to their ability to safely withstand the pressures involved. Figure 2 illustrates their relative dimensions. They were designed to permit of three measurements in each of the following temperature intervals: D, +15 to 50° C.; E, -40 to +20° C.; F, -50 to 0° C.

*Balance and weighing chamber.*—The balance used in the calibration of the picnometers and in the determinations of the mass of ammonia was made by A. Collot, Paris. It was equipped with air dashpots to make the swings practically aperiodic. The picnometers were suspended in a closed chamber directly beneath the balance by means of small rods connected to the scale pans. Weighings could be made to about 0.1 mg. The weights used in all the weighings were calibrated by the weights and measures division of this bureau and corrections given to 0.01 mg.

*Thermoregulated bath.*—The thermoregulated bath used in all of the measurements was contained in a cylindrical Dewar flask of about 6 liters capacity. The temperature-regulating mechanism was assembled as a unit in a long, cylindrical brass tube about one-quarter the diameter of the flask, so as to leave more than three-quarters of the useful area available for the introduction of the picnometers. This regulating unit included a motor-driven direct-connected screw-propeller stirrer, electric heating coil, carbon dioxide expansion cooling coil, and a toluene-filled thermoregulator which served to maintain the temperature constant to about 0.01° C. The details of the construction of a similar unit have been described previously.<sup>10</sup> The liquid used in the bath was a mixture of about 65 per cent carbon tetrachloride and 35 per cent gasoline, a mixture selected with reference to fluidity and transparency at temperatures down to -50° C., combined with maximum safety from fire hazard when at room temperature or

<sup>10</sup> N. S. Osborne, B. S. Bulletin, 14, p. 145; 1917; (Scientific Paper No. 301); Amer. Soc. Refrig. Eng. Jour., 4, p. 118; 1917.



warmer. The volatile hydrocarbons which meet the greatest number of requirements of a low-temperature bath are not safe alone in proximity to electric motors and heating circuits which may possibly spark, but the admixture of a large carbon tetrachloride content makes the fluid entirely safe in this respect and does not destroy transparency to a serious degree, provided reasonable precautions are taken to exclude atmospheric moisture. The flash point of this mixture was about  $+50^{\circ}\text{C}$ . One disadvantage of this mixture is its corrosive effect on some metals, particularly copper. The corrosion was not serious, however, in the present application except that the transparency of the liquid was reduced after several months of service and necessitated an occasional renewal of the bath liquid. As a protection to the observer in case of failure of the picnometers under pressure and also failure of the Dewar flask itself, the bath was inclosed in a metal case which was provided with celluloid windows about 3 mm in thickness.

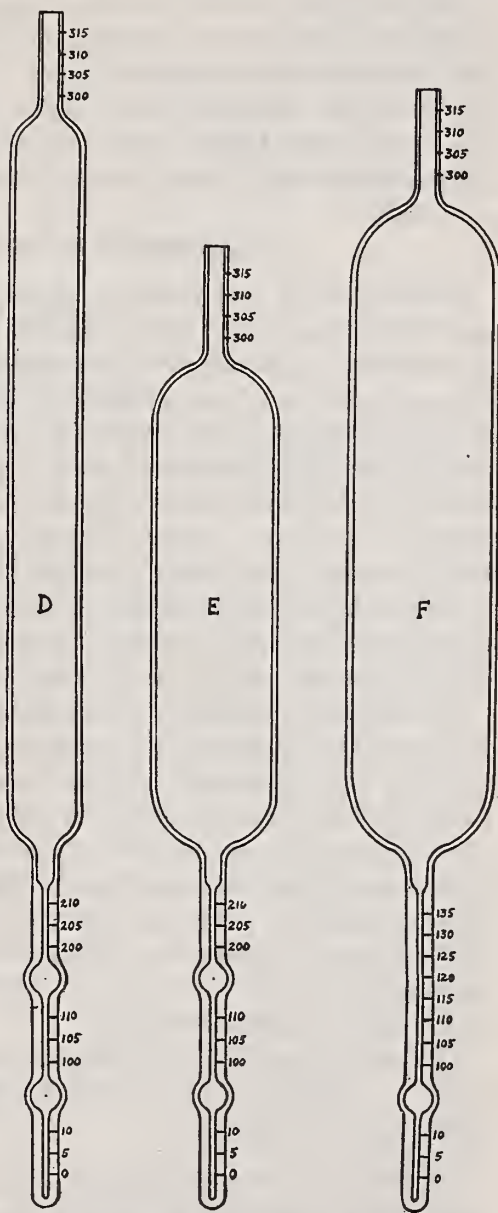


FIG. 2.—Sketch of picnometers, showing relative dimensions and position of arbitrary scaling (Tables 3 and 5).

*Thermometers.*—Mercurial thermometers, graduated in tenth degrees, were used over the temperature interval  $-30$  to  $+50^{\circ}\text{C}$ .

These thermometers were calibrated against platinum resistance thermometers at  $5^{\circ}$  intervals. Platinum resistance thermometers of the four-lead potential terminal type, with strain-free winding, previously described by Waidner and Burgess,<sup>11</sup> were used in all the temperature measurements below  $-30^{\circ}\text{C.}$  and also in conjunction with the mercurial thermometers at higher temperatures. The Wheatstone bridge used in connection with the resistance thermometers was of the four-dial type and has been described previously.<sup>12</sup>

## 2. CALIBRATION OF PICNOMETERS.

Distilled water and mercury, which had been purified by the electrolytic process and by distillation, were used in the volumetric calibrations. Volumes were determined by observing the level of the meniscus at a given temperature, usually  $+20^{\circ}\text{C.}$ , weighing in air, and multiplying the observed weight by the factor given in the Landolt and Börnstein tables of physical and chemical constants which contains the buoyancy and specific volume corrections.<sup>13</sup> The lower portion of each picnometer was calibrated with mercury before being attached to the large bulb. The final volumes adopted were obtained from the mean of several mercury calibrations plus the calculated correction for the difference in volume between concave and convex menisci.<sup>14</sup>

The pressure coefficient of expansion of each picnometer was determined by applying air pressure from a cylinder of compressed air with the picnometer almost completely filled with water. Readings were taken on the upper tube at intervals of five atmospheres up to a pressure of about three times the maximum pressure to be encountered in actual use. The value for the compressibility of water at  $20^{\circ}\text{C.}$  was taken as  $45 \times 10^{-6}$  per atmosphere.<sup>15</sup> The temperature coefficient of volume expansion of the glass was assumed to be  $26 \times 10^{-6}$  per  $^{\circ}\text{C.}$  These factors enter into the results only as small corrections.

The final results of the picnometer calibrations are given in Table 3. Interpolation was effected by the use of the factors, volume per scale division.

<sup>11</sup> B. S. Bulletin, 6, p. 154; 1910 (Scientific Paper No. 124).

<sup>12</sup> B. S. Bulletin, 13, p. 547; 1916 (Scientific Paper No. 288).

<sup>13</sup> Although the Landolt-Börnstein tables are labeled cubic centimeters, the factor given actually reduces volumes to milliliters rather than to cubic centimeters, but the difference in the two units is insignificant for the results of work described in this paper. The volume of 1 g of water at  $4^{\circ}\text{C.}$ , defined as 1 ml ( $=1.000027\text{ cm}^3$ ), differs from a cube of 1 cm edge by about 27 parts in 1,000,000.

<sup>14</sup> Discussed in paper on Specific Volume of Liquid Ammonia; B. S. Scientific Papers, 17, p. 287; 1921 (Scientific Paper No. 420); Jour. Amer. Soc. Refrig. Eng., 7, p. 113; 1920.

<sup>15</sup> Bridgman, Proc. Amer. Acad. Arts and Sciences, 48, p. 341; 1912.

TABLE 3.—Final Results of Picnometer Calibrations.

Picnometer.	Volume in cubic centimeters to scale division—				Volume per scale division in cubic centimeters.	Increase in volume per unit volume per atmosphere.
	5	105	205	310		
D.....	0.0491	1.0485	1.5535	89.09	0.00440	0.000012
E.....	.0312	1.0354	1.5492	175.04	.00324	.000021
F.....	.0449	1.7577	.....	399.64	.00473	.000035
	0	20	40	310		
F <sup>1</sup> .....	.0345	.0959	.1571	358.31	.00306	.000035
	10	40	60	310		
F <sup>2</sup> .....	.0268	.1265	.1928	353.74	.00334	.000035

<sup>1</sup> Calibration applies to first series in test for adsorption.<sup>2</sup> Calibration applies to second series in test for adsorption.

### 3. PURIFICATION OF SAMPLES AND METHOD OF FILLING PICNOMETERS.

The ammonia used in these measurements was prepared by two methods, described more in detail in an independent paper.<sup>16</sup> Only a brief description of the processes of purification will therefore be given here.

*Method 1.*—Commercial ammonia in which no traces of pyridine or ammonium acetate could be detected chemically and which showed a very small residue on evaporation was used as the starting material. This material was converted into ammonium sulphate by passing the gas into sulphuric acid after it had passed through a tube containing lime heated to a red heat. The ammonium sulphate solution obtained was heated with sodium hydroxide and the ammonia gas thus liberated. The gas was dried by passing it through an all-glass train of potassium hydroxide, previously ignited lime, and barium oxide, and was then condensed in a glass bulb cooled with a mixture of solid carbon dioxide and petroleum ether. The ammonia was then fractionally distilled several times, frozen with liquid air repeatedly, and then frozen by its own evaporation, the vapor being pumped off through a vacuum pump. The final products obtained by the above procedure are designated in Table 5 as Samples G and H.

*Method 2.*—A sample of synthetic ammonia, made by the Haber process, was used as the starting material. This was transferred by distillation into a small steel container which would hold about a kilogram. The first portion was discarded, and the middle portion distilled into a similar vessel containing metallic sodium, in

<sup>16</sup> E. C. McKelvy and C. S. Taylor; Composition, Purification, and Certain Constants of Ammonia, B. S. Scientific Papers, 18, p. 655; 1923 (Scientific Paper No. 465); Refrigerating Engineering, 9, p. 213; 1923.



the form of a fine wire, to remove any traces of water. Following this dehydration the liquid was distilled into a high-pressure fractional-distillation apparatus and fractionally distilled eight times, rejecting the first and last fractions (a little less than one-tenth the total volume of the liquid) in each distillation. The product thus obtained was distilled into a vacuum-fractional distillation apparatus of glass and fractionally distilled about 10 times, the first and last portions being rejected in each case. The ammonia was then frozen in liquid air and the residual vapor and gas pumped off. The ammonia was then allowed to warm up until it was entirely liquid and some of the vapor was escaping through a mercury seal. It was again frozen in liquid air and the vapor pumped off as before. This process was repeated several times. Finally the ammonia was frozen into small flocculent crystals by its own evaporation, the resulting vapor being pumped off and discarded. This final product, designated Sample I in Table 5, was used for filling the picnometers. Samples designated K and L, were also made by this method, with the exception that a commercial sample, the same as the one used in method 1, was used as a starting material.

The tests for purity on the final samples of ammonia obtained by the above methods gave the following results: Water, less than 0.003 per cent, by weight, which was the limit of sensitivity of the chemical test applied; noncondensing gases, from approximately 1 part in 10,000 to 1 part in 1,000,000 by volume, for different samples.

The picnometers were cleaned with a mixture of concentrated nitric and sulphuric acids, aqueous potassium hydroxide solution, and washed with distilled water. The upper end of each picnometer was always constricted, so as to facilitate a satisfactory seal, and a small auxiliary bulb was attached by means of a glass T. The function of this bulb was to permit the last distillation to be made in a closed system, thus avoiding the possibility of mercury vapor and impurities from stopcocks being distilled into the picnometers. After being sealed directly into the glass line of the vacuum distillation apparatus the picnometers were heated to about 250° C. in a bath of glycerine and evacuated to a pressure less than 0.0001 mm of mercury for a considerable time to remove from the walls as completely as possible all occluded gases and particularly water vapor. A sufficient quantity of the purified ammonia was then distilled into one of the auxiliary bulbs, the supply reservoir cut off, and the ammonia



frozen by means of liquid air. The vapor phase was pumped off with the aid of a high-vacuum pump, and the picnometer, together with its auxiliary bulb, was removed from the distillation apparatus by fusing the connecting tube. Commercial liquid ammonia in an open Dewar flask was used to cool the lower portion of the picnometer during the last distillation. When approximately the desired amount of ammonia had been distilled into the picnometer, the auxiliary bulb and the lower portion of the picnometer were immersed in liquid air and the picnometer sealed by fusing the constricted capillary.

#### 4. PROCEDURE IN DETERMINATIONS.

For a determination of the specific volume at any given temperature the three necessary quantities (see equation 2) are the total volume of the picnometer, the total mass of ammonia, and the volume of the liquid in equilibrium with its vapor at that temperature. The total volume of the picnometer was obtained by adding to its calibration at the highest scale division visible the estimated volume of the tip, formed in the process of sealing off, and correcting for the particular pressure and temperature of the experiment. The total mass of ammonia in the picnometer was a constant during any series of measurements and was always determined afterwards by weighing the picnometer and its contents, then breaking the tip, and reweighing filled with dry air. The volume of the liquid in equilibrium with its vapor was observed at various temperatures by reading the position of the meniscus upon the previously calibrated capillary scales.

The certainty with which the latter observation could be made was largely a function of the time spent and of the patience of the observer. Hours and often days were required to obtain one observation. It was necessary to maintain the temperature of the bath constant for hours at a time, and variations in the electric power or the rate of cooling or the nonfunctioning of the thermostat mechanism would often ruin the chance of an observation for the day. The procedure followed was to first determine approximately the temperature at which the liquid appeared in one of the capillaries. The temperature of the bath was then maintained constant with a falling meniscus, which indicated that the vapor was unsaturated. With a little experience it was possible to estimate the true equilibrium temperature from the observed rate of evaporation. The bath temperature was lowered the estimated amount in order to hasten the attainment of equi-

librium, and readings were taken at successive time intervals. The test for equilibrium adopted was that the position of the meniscus should remain constant to one-tenth of a scale division for a period of one hour.

(a) DETERMINATION OF MASS OF AMMONIA.—A short deep scratch was made at the tip of the picnometer with a diamond, or a special glass-cutting tool. The external surface of the picnometer was then cleaned with chromic acid, water, and acetone successively. After being permitted to hang in the weighing chamber for nearly an hour in order to come to temperature equilibrium it was weighed independently by two observers. In all of the weighings a counterpoise of equal external volume was employed and weighings made by substitution. The lower portion of the picnometer was cooled with a mixture of solid carbon dioxide and gasoline until the pressure inside was less than atmospheric, and by applying a heated glass rod the tip was broken carefully, so as to lose no glass by splintering. The picnometer was then heated in water and evacuated several times to remove all trace of ammonia vapor. It was finally filled with dry air, cleaned, and reweighed, as before, by two observers.

In the earlier measurements an attempt was made to obtain a check on the total mass by absorbing the ammonia in a flask of sulphuric acid of known weight. The mass determined in this manner was consistently lower by about 1 or 2 parts in 1,000 than that determined by the method of direct weighing, which was probably due to the action of ammonia on the rubber tubing used to connect the picnometer and acid flask. No weight was given in the final results to the mass determinations by this method.

(b) SUPERHEATING OF VAPOR.—In the preliminary experiment it became evident that precautions were necessary to prevent the condensation of ammonia on the walls of the bulb. Equilibrium was never attained in those preliminary experiments because of the local cooling of the portion of the picnometer nearest the carbon-dioxide cooling coil. Condensation in the form of small droplets which grew larger with time was observed on that portion of the walls of the picnometer. To avoid this difficulty, the bulb of the picnometer was inclosed in a brass cylinder upon which was wound an electric heating coil. This permitted a slight heating of the bath liquid in its upward path around the bulb. The temperature difference between the bulb

and the lower portion of the picnometer was observed by means of five copper-constantan thermocouples. The warm junctions were attached to the bulb in various localities to integrate its temperature as well as possible, and the cold junctions were attached to the capillary containing the free surface of the liquid ammonia. The electric energy supplied was adjusted until each couple indicated a difference in temperature of a few hundredths of a degree. The mean of the thermocouple indications was taken as a measure of the superheat of the vapor.

(c) SURFACE ADSORPTION.—The phenomenon of adsorption of gases on glass surfaces is well known, but quantitative data on the amount of adsorption are very difficult to obtain. Keyes and Brownlee<sup>17</sup> have stated that "ammonia is adsorbed on glass surfaces to a more marked extent than any other gas." They attribute this to the fact that ammonia is very soluble in water, which is known to be adsorbed and difficult to remove from glass surfaces.

The best means of noting the effect of adsorption in the present measurements seemed to be to increase the ratio of surface area to volume. For this purpose a "seven-fingered" picnometer was made, in which this ratio was doubled. This picnometer consisted of six tubes about 1.5 cm in diameter attached to a similar central tube. It was found very difficult to attain equilibrium with this picnometer and to be certain that the central tube was free from condensation. The desired result was better accomplished by filling two of the original picnometers with a large number of thin glass tubes about 2 or 3 mm in diameter. The approximate surface areas of the picnometers and the inclosed tubes were calculated as shown in the following table.

TABLE 4.—Surface Area (in Square Centimeters) of Picnometer.

D	E	F	E+tubes.	F+tubes.
130	220	390	2,900	4,070

It may be noted that the surface was increased by a factor of 13 in one case and 10 in the other.

##### 5. RESULTS OF MEASUREMENTS.

The results of the measurements by the direct method are given in Table 5. A number of preliminary experiments in which no provision was made for superheating the vapor and which

<sup>17</sup> Thermodynamic Properties of Ammonia, p. 21 (John Wiley & Sons); 1916.



are, therefore, uncertain as to dryness of walls have not been included. Only those experiments in which equilibrium was well established have been included.

TABLE 5.—Measurements of the Specific Volume of Saturated Ammonia Vapor.

## PICNOMETER D.

Date.	Sam- ple.	Read- ing of menis- cus scale divi- sions.	Volume of liquid. $v$	Mass of liquid. $\frac{v}{u}$	Total mass of am- monia. $M$	Mass of vapor. $M - \frac{v}{u}$	Volume of vapor. $V - v$	Aver- age super- heat.	Tem- pera- ture.	Specific volume. $u'$	Devia- tion from equa- tion.
			cm <sup>3</sup>	g	g	g	cm <sup>3</sup>	°C.	°C.	cm <sup>3</sup> /g	Per cent.
Mar. 25, 1918	K	103.9	1.0441	0.6182	1.4637	0.8455	88.25	0.08	+32.03	104.37	-0.01
Mar. 26, 1918	K	8.4	.0647	.0364	1.4637	1.4273	89.28	.06	+50.53	62.55	-0.02
Mar. 27, 1918	K	203.0	1.5445	.9520	1.4637	.5117	87.71	.04	+15.56	171.41	-0.20
Feb. 18, 1919	L	7.8	.0619	.0352	1.3078	1.2726	89.21	.03	+46.32	70.10	-0.10
Feb. 28, 1919	L	107.4	1.0592	.6401	1.3078	.6677	88.15	.05	+24.05	132.00	-0.04

## PICNOMETER E.

July 13, 1916	G	7.8	0.0403	0.0246	1.2154	1.1908	175.11	0.05	+20.53	147.05	+0.02
July 17, 1916	G	107.0	1.0413	.6690	1.2154	.5464	173.99	.04	-2.85	318.43	-0.75
Oct. 28, 1916	G	7.8	.0403	.0246	1.2100	1.1854	175.09	.05	+20.37	147.71	-0.03
Nov. 1, 1916	G	208.1	1.5577	1.0655	1.2100	.1445	173.29	.15	-35.19	1,199.20	-2.18
Nov. 2, 1916	G	107.5	1.0430	.6704	1.2100	.5396	173.96	.09	-3.09	322.39	-0.36
Jan. 22, 1917	H	207.0	1.5549	1.0192	1.3939	.3747	173.39	.08	-12.67	462.74	-0.37
Jan. 23, 1917	H	108.8	1.0474	.6607	1.3939	.7332	173.97	.12	+5.68	237.27	-0.22
Jan. 25, 1917	H	9.2	.0448	.0270	1.3939	1.3669	175.10	.04	+25.07	128.09	+0.02
Jan. 29, 1917	H	206.2	1.5521	1.0171	1.3939	.3768	173.39	-----	-12.54	460.16	-0.31
Jan. 30, 1917	H	107.6	1.0435	.6580	1.3939	.7359	173.97	.02	+5.79	236.40	-0.21
Mar. 29, 1917	H	207.9	1.5580	1.0152	1.4356	.4204	173.51	.05	-9.70	412.73	-0.24
Apr. 2, 1917	H	108.0	1.0448	.6564	1.4356	.7792	174.13	.07	+7.47	223.47	-0.14
Apr. 3, 1917	H	107.4	1.0429	.6551	1.4356	.7805	174.14	.05	+7.55	223.11	-0.06
May 25, 1917	I	207.7	1.5561	1.0726	1.1895	.1169	173.30	.03	-39.44	1,482.55	-1.71
May 26, 1917	I	106.0	1.0381	.6686	1.1895	.5209	173.99	.01	-4.05	334.02	-0.29
June 6, 1917	I	10.0	.0474	.0290	1.1895	1.1605	175.11	-----	+19.67	150.89	-0.09
July 9, 1917	I	6.1	.0348	.0211	1.3272	1.3061	175.16	.03	+23.53	134.11	-0.06
July 11, 1917	I	108.8	1.0474	.6649	1.3272	.6623	174.04	-----	+2.76	262.78	-0.01
Aug. 9, 1917	I	209.4	1.5627	1.0375	1.3272	.2897	173.42	.12	-19.20	598.62	-0.89
Aug. 10, 1917	I	203.4	1.5425	1.0215	1.3272	.3057	173.45	.07	-17.88	567.39	-0.76

## PICNOMETER F.

Sept. 30, 1916	G	107.9	1.7691	1.2031	1.5786	0.3755	397.24	0.04	-32.02	1,057.80	-0.15
Oct. 2, 1916	G	128.3	1.8680	1.2824	1.5786	.2962	397.09	.04	-37.23	1,340.60	-0.92
Oct. 2, 1916	G	134.3	1.8961	1.3056	1.5786	.2730	397.05	.05	-38.92	1,454.40	-1.00
Oct. 3, 1916	G	10.0	.0686	.0435	1.5786	1.5351	399.31	.02	+2.98	260.12	-0.27
Nov. 11, 1916	G	8.0	.0591	.0376	1.5030	1.4654	399.46	.02	+1.94	270.26	-0.11
Dec. 2, 1916	G	105.0	1.7552	1.2051	1.5030	.2979	397.34	.07	-37.29	1,333.80	-1.66
Dec. 6, 1916	G	111.0	1.7834	1.2277	1.5030	.2753	397.31	.04	-38.77	1,443.20	-1.04
Jan. 9, 1917	H	134.0	1.8945	1.3118	1.5441	.2323	397.08	.08	-42.07	1,709.30	-0.68
Jan. 13, 1917	H	102.6	1.7440	1.1888	1.5441	.3553	397.32	.08	-33.29	1,115.10	-0.49
Feb. 2, 1917	H	101.4	1.7383	1.1843	1.5441	.3598	397.32	-----	-32.99	1,104.30	-0.06
Feb. 6, 1917	H	121.1	1.8346	1.2615	1.5441	.2826	397.18	-----	-38.13	1,405.40	-0.55
Mar. 1, 1917	H	135.6	1.9016	1.3266	1.5142	.1876	396.93	.06	-46.42	2,115.80	-1.97
Mar. 20, 1917	H	135.2	1.8997	1.3251	1.5142	.1891	396.93	.09	-46.33	2,099.00	-2.37
Mar. 22, 1917	H	101.1	1.7368	1.1884	1.5142	.3258	397.21	.05	-35.36	1,219.20	-1.33
Mar. 23, 1917	H	102.2	1.7454	1.1949	1.5142	.3193	397.21	.05	-35.57	1,244.00	-0.35
Mar. 24, 1917	H	7.9	.0586	.0373	1.5142	1.4769	399.27	.02	+1.85	270.41	-0.25
Mar. 26, 1917	H	122.0	1.8384	1.2714	1.5142	.2428	397.04	-----	-41.36	1,635.30	-1.46
Apr. 27, 1917	I	126.0	1.8567	1.2992	1.4681	.1689	397.27	.15	-48.19	2,352.10	-0.86
May 2, 1917	I	130.7	1.8785	1.3205	1.4681	.1476	397.22	.19	-50.87	2,691.20	-2.18
May 3, 1917	I	129.0	1.8707	1.3130	1.4681	.1551	397.24	.33	-50.00	2,561.20	-1.53
May 10, 1917	I	126.0	1.8567	1.2996	1.4681	.1685	397.27	.17	-48.32	2,357.70	-1.36
May 14, 1917	I	128.7	1.8693	1.3118	1.4681	.1563	397.24	.09	-49.86	2,541.50	-2.26
May 18, 1917	I	106.0	1.7597	1.2151	1.4681	.2530	397.45	.05	-40.49	1,570.90	-1.23
May 21, 1917	I	9.9	.0681	.0434	1.4681	1.4247	399.58	.07	+0.84	280.47	-0.22



TABLE 5.—Measurements of the Specific Volume of Saturated Ammonia Vapor—Continued.

## PICNOMETER F FILLED WITH THIN-WALLED CAPILLARY TUBES.

Date.	Sam- ple.	Read- ing of menis- cus scale divi- sions.	Volume of liquid. $v$	Mass of liquid. $\frac{v}{u}$	Total mass of am- monia. $M$	Mass of vapor. $M - \frac{v}{u}$	Volume of vapor. $V - v$	Aver- age super- heat.	Tem- pera- ture.	Specific volume. $u'$	Devia- tion from equa- tion.
			cm <sup>3</sup>	g	g	g	cm <sup>3</sup>	°C.	°C.	cm <sup>3</sup> /g	Per cent.
July 3, 1917	I	39.4	0.1549	0.1085	0.2605	0.1520	357.76	0.03	-48.51	2,353.70	-2.52
July 3, 1917	I	12.7	.0734	.0508	.2605	.2097	357.89	.04	-42.38	1,706.70	-2.40
July 5, 1917	K	4.2	.0473	.0327	.2605	.2278	357.93	.05	-40.57	1,571.20	-1.50
May 1, 1918	K	19.8	.0594	.0409	.2857	.2448	358.67	.35	-38.92	1,465.20	-.51
May 6, 1918	K	48.8	.1551	.1080	.2857	.1777	358.53	.30	-45.41	2,019.61	-1.35
May 7, 1918	K	40.0	.1268	.0880	.2857	.1977	358.57	.21	-43.22	1,813.70	-1.60

## PICNOMETER E FILLED WITH THIN-WALLED CAPILLARY TUBES.

Apr. 10, 1918	K	2.9	0.0243	0.0154	0.5109	0.4955	131.76	0.06	+2.42	265.91	-0.09
Apr. 11, 1918	K	3.0	.0246	.0156	.5109	.4953	131.76	.10	+2.42	266.03	-.05

The values for the specific volume of the liquid used in correcting for the mass of the liquid were taken from the measurements made at this bureau and published in a separate paper.<sup>18</sup> The correction for the superheat of the vapor is small and has not been applied to these measurements. To a first approximation superheating the vapor increases the specific volume in proportion to the absolute temperature. Thus, one-tenth of a degree superheat would amount to a correction of about 1 part in 3,000. In most cases the amount of superheat was less than 0.1° C.

The scale of temperature used in these measurements is the scale defined by the resistance thermometer of pure platinum, calibrated in ice, steam, and sulphur vapor (444.6° C. taken as the normal boiling point of sulphur). Using the Callendar equation

$$t = \frac{R_t - R_0}{R_{100} - R_0} 100 + \delta \left( \frac{t}{100} - 1 \right) \frac{t}{100}$$

as an interpolation equation, the temperature scale so defined represents the centigrade thermodynamic scale in the interval -50 to +450° C. to the accuracy with which that scale is at present known and has been adopted as the standard working scale of the Bureau of Standards in that interval.

## IV. OPTICAL METHOD.

The close relation between the refractive index of a substance and its density has been the subject of considerable study, theo-

<sup>18</sup> B. S. Scientific Papers, 17, p. 287; 1921 (Scientific Paper No. 420).

retically as well as experimentally, in the past. The empirical relation  $\frac{n-1}{d} = \text{constant}$ , where  $n$  represents the refractive index and  $d$  the density, was first proposed by Gladstone and Dale<sup>19</sup> and has been found to hold for gases at moderate pressures within the accuracy of the measurements. L. Lorenz<sup>20</sup> and later H. A. Lorentz<sup>21</sup> deduced independently, from the elastic solid theory and the electron theory, respectively, the relation  $\frac{n^2-1}{(n^2+2)d} = \text{constant}$ . This relation has been tested by experiments with air at pressures up to 176 atmospheres by Magri,<sup>22</sup> with various fluids in the liquid and gaseous states by L. Lorenz<sup>20</sup> and Bleekrode,<sup>23</sup> and with carbon dioxide above its critical temperature by Phillips.<sup>24</sup>

The difference between the two above equations can hardly be distinguished by measurements with gases at low pressures. The experimental evidence in support of these relations, a summary of which is given by Matthews,<sup>25</sup> suggested a method of comparing under various conditions the specific volume of a vapor, which method it was hoped would yield more consistent and possibly more accurate results than those obtained by the direct method.

By definition the index of refraction  $n$  of any medium for wave length  $\lambda$  is

$$n = \frac{\text{velocity of light of wave length } \lambda_0 \text{ in vacuum}}{\text{velocity of light of wave length } \lambda_m \text{ in medium}}$$

In either case the velocity is the product of wave length and frequency, and since the frequency is assumed to remain constant we may write

$$n = \frac{f \cdot \lambda_0}{f \cdot \lambda_m} = \frac{\lambda_0}{\lambda_m} \quad (1)$$

The apparatus here used for the measurement of  $n$  is the Fizeau-Pulfrich interferometer, which consists of two nearly parallel

<sup>19</sup> Phil. Trans., 151, p. 317; 1863.

<sup>20</sup> Wied. Ann., 11, p. 70; 1880.

<sup>21</sup> Theory of Electrons (Teubner, Leipzig); 1909.

<sup>22</sup> Phys. Zeit., 6, p. 629; 1905. (H. A. Lorentz points out in "Theory of Electrons" that Magri's results agree well with his formula.)

<sup>23</sup> Proc. Roy. Soc., 37, p. 339; 1884.

<sup>24</sup> Proc. Roy. Soc., 97, p. 225; 1920. Working with carbon dioxide at 34° C., Phillips found the constant in the Lorenz-Lorentz relation decreased about 1 per cent at high densities (corresponding pressures about 400 atmospheres). This is the only experimental work known to the authors in which the deviations from the Lorenz-Lorentz relation were not well within the limit of experimental error. The evidence in this case is not entirely conclusive, since the observed systematic deviation might have been due to a variable adsorbed film of gas on the interferometer plates. The presence of such a film in the case of ammonia is suggested in the text of the present paper. With a gas in the neighborhood of its critical temperature and at pressures greater than its critical pressure it is conceivable that the thickness of such a film might become appreciable compared with the wave length of visible light.

<sup>25</sup> Jour. Franklin Inst., 177, p. 673; 1914.

plates rigidly supported about 1 cm apart. When the space between the plates is evacuated, the distance  $e$  between the plates is found to contain  $W_o$  waves of length  $\lambda_o$ . When ammonia vapor at a definite temperature and pressure is present between the plates,  $W_m$  waves of length  $\lambda_m$  are found to be contained in the same distance  $e$ . Since  $e$  is a constant, we have

$$e = W_o \lambda_o = W_m \lambda_m \quad \text{or} \quad \frac{\lambda_o}{\lambda_m} = \frac{W_m}{W_o}$$

Thus, from equation (1)

$$n = \frac{\lambda_o}{\lambda_m} = \frac{W_m}{W_o} \quad \text{and} \quad n - 1 = \frac{W_m - W_o}{W_o}$$

The number of waves  $W_o$  between the plates under vacuum conditions is approximately a constant for a given interferometer and is obtained with sufficient accuracy in the present case by dividing the measured distance between the plates by the wave length of the light used. The change in the total number of waves ( $W_m - W_o$ ) in passing from vacuum to vapor is observed by measuring the accompanying shift of the interference fringes.

#### 1. DESCRIPTION OF APPARATUS.

The interferometer plates and separating strut were made of fused silica. This strut was made from a tube which was about 1 cm long and 2 cm in diameter and was ground until the end surfaces were nearly parallel to one another. A portion of the material was then cut away, leaving three triangular areas as bearing points at each end. The plates were fused to the separating tube at each of these bearing points by heating with a small oxyhydrogen flame and adding a small globule of silica. This is a very desirable feature, because it adds greater stability to the interferometer which is much less liable to get out of adjustment by slight vibrations and accidental jars. It also precludes the possibility of the presence of varying films of vapor beneath these bearing points which is often a source of difficulty in accurate measurements with this type of interferometer.

The interferometer shown in Figure 3 was inclosed in a pyrex glass tube and was supported by a short piece of steel tubing coated with tin. One end of this supporting tube was notched and spread so that it fitted snugly in the glass tube. A window of pyrex glass about 1 cm thick with plane surfaces was sealed near the center of the tube. The space between this window and the one at the top of the tube was filled with dry air.



The Pulfrich apparatus,<sup>26</sup> a portion of which is shown in Figure 3—namely, the prism *P* and lens *O*—contains a helium lamp for illuminating the interferometer and the optical arrangement necessary for measuring the displacement of the fringes. This apparatus was equipped with a set of movable double cross

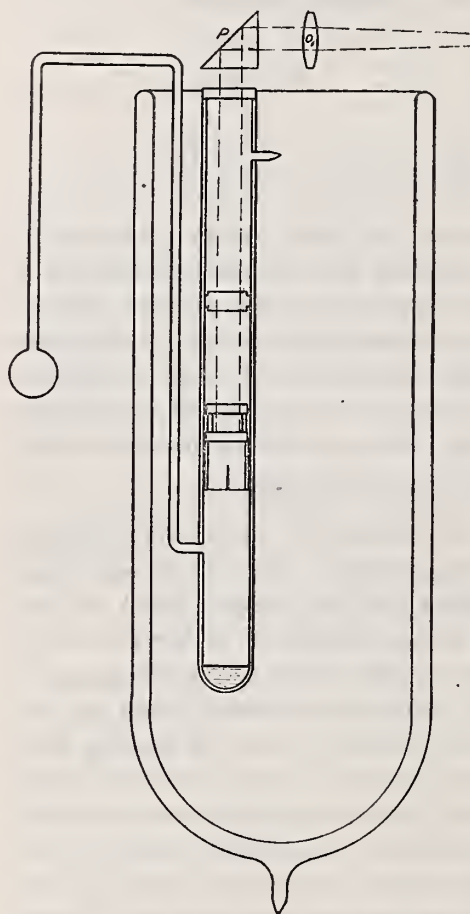


FIG. 3.—Sketch of refractometer and Dewar flask, used as a thermoregulated bath in both methods.

hairs attached to a screw with a circular head graduated in degrees. The fractional part of a fringe width represented by the distance from a small reference circle ruled on one of the interferometer plates could be measured within about 0.02 or 0.03 of a fringe.

## 2. EXPERIMENTAL PROCEDURE.

The linear expansion of the silica strut was measured over the temperature interval  $-50$  to  $+50^{\circ}$  C. with the system evacuated. This expansion, which is small (equivalent to about one fringe over the above temperature interval), was not measured with precision, since it entered into the results only as a small correction. Ammonia of high purity was then distilled into the small bulb, frozen with liquid air, and the apparatus sealed by fusion of the connecting glass tube.

The relatively poor thermal contact of the interferometer plates with the bath liquid made it impossible to work with a rise in the temperature of the bath. In such cases ammonia was condensed on the plates, destroying the interference pattern. The procedure followed was to start at about room temperature, taking measure-

<sup>26</sup> Zeit. für Instrumentenkunde, 18, p. 261; 1898.



ments of the fringe shifts by lowering the temperature in intervals of 5 or 10°. The lag in the temperature of the interferometer plates kept them dry. After the bath had been regulated at a constant temperature (within 0.01° C.) for a period of about one-half hour condensation began to take place on the plates. It was necessary, therefore, to take measurements soon after making the temperature regulation, and the vapor between the plates was undoubtedly superheated. The amount of this superheat was not measured, but probably was not more than a few tenths of a degree. Readings on the fringe fraction at each step were taken over a period of about 15 minutes and were remarkably constant. The final readings were made with vacuum between the plates, which was accomplished by condensing and freezing the ammonia in the outer bulb with liquid air. The pressure then existing was of the order of 0.001 mm.

### 3. RESULTS OF MEASUREMENTS.

Several measurements of the index of refraction of ammonia vapor at 0° C. and 760 mm pressure were made, the results of which are shown in Table 6. The pressures in these experiments were measured with a mercury manometer about 2 cm in diameter and a cathetometer. The density of ammonia under these conditions was taken as 0.7708 g per liter, which is the result obtained by Perman and Davies,<sup>27</sup> and Guye and Pintza,<sup>28</sup> and is probably correct within 0.1 per cent. The constant in the Gladstone and Dale relation was found to be 0.4970. This was used in calculating the specific volume from the refractive index measurements.

TABLE 6.—Index of Refraction of Ammonia Vapor at 0° and 760 mm for Wave Length  $\lambda=5876 \text{ \AA}$ .

$$[d=0.0007708 \text{ g/cm}^3 \quad \frac{n-1}{d}=0.4970]$$

Date.	Pressure in millimeters of mercury at 0° and standard gravity.	Fringe shift observed.	$n-1$ at 0° and 760 mm.
1918.			
Mar. 7.....	757.8	12.279	0.0003832
Mar. 8.....	758.8	12.316	.0003839
Mar. 10.....	757.0	12.282	.0003837
Mar. 11.....	761.6	12.324	.0003827
Do.....	759.3	12.284	.0003826
Do.....	761.4	12.316	.0003826
Do.....	758.6	12.272	.0003826
Mar. 13.....	761.4	12.356	.0003838
Do.....	761.4	12.341	.0003833
Do.....	756.9	12.255	.0003829
Mar. 29.....	755.0	12.229	.0003831
Do.....	771.2	12.502	.0003834
Do.....	758.8	12.288	.0003830
Do.....	760.9	12.329	.0003832
Mean.....			.0003831

<sup>27</sup> Proc. Roy. Soc., 78A, p. 28; 1906.

<sup>28</sup> Comptes Rendus, 141, p. 51; 1905.

The results of the measurements on the index of refraction of the saturated vapor, together with the calculated specific volumes, are given in Table 7. Corrections have been applied for the expansion of the silica strut (always less than 0.5 per cent) and also for its compression with pressure (about 0.03 fringe per atmosphere), using the value for compressibility as determined by Adams, Williamson, and Johnston.<sup>29</sup>

TABLE 7.—Specific Volume Calculated from Measured Index of Refraction.<sup>1</sup>

Date.	Temperature.	Fringe shift observed.	$(n-1)10^7$	$n'$	Deviation from equation.	Deviation expressed in fraction of fringe.
1918.	° C.			cm <sup>3</sup> /g	Per cent.	
June 30.....	-0.33	54.35	16,927	293.61	+0.33	0.19
	- .66	53.65	16,709	297.44	+ .25	.14
	-1.25	52.54	16,363	303.73	+ .33	.17
	-10.55	37.22	11,592	428.74	+ .32	.12
	-20.53	24.95	7,774	639.3	+ .28	.07
	-29.76	16.65	5,185	958.5	+ .66	.11
	-40.67	9.89	3,080	1,613.6	+ .65	.06
	-49.76	6.09	1,897	2,619.9	+1.35	.08
	-49.93	6.05	1,884	2,638.0	+1.06	.06
July 1.....	+ .42	55.77	17,369	286.14	+ .26	.15
	-10.44	37.33	11,626	427.5	+ .43	.16
	-19.82	25.68	7,998	621.4	+ .32	.09
	-29.97	16.49	5,136	967.7	+1.13	.18
	-41.34	9.54	2,971	1,672.8	+ .87	.08
	-50.94	5.73	1,785	2,784.3	+1.50	.09
July 2.....	+19.61	105.35	32,810	151.48	+ .13	.14
	+15.61	92.92	28,939	171.74	+ .10	.09
	+10.37	78.39	24,414	203.57	+ .16	.13
	+5.41	66.36	20,667	240.48	+ .18	.12
	+ .29	55.51	17,288	287.48	+ .28	.15
	-19.76	25.70	8,004	620.9	+ .53	.14
July 3.....	+26.63	130.46	40,630	122.32	+ .06	.08
	+24.94	123.97	38,609	128.73	+ .13	.16
	+22.30	114.49	35,657	139.38	+ .10	.11
	+19.93	106.39	33,134	150.00	+ .15	.16
	+15.00	91.07	28,363	175.23	+ .15	.14
	+9.84	76.97	23,972	207.33	+ .22	.17
	+5.50	66.53	20,720	239.86	+ .25	.17
	+ .25	55.42	17,260	287.95	+ .29	.16
	-9.67	38.50	11,990	414.51	+ .30	.12
	-19.88	25.55	7,957	624.6	+ .60	.15
	-29.69	16.65	5,185	958.5	+ .99	.17
	-40.29	10.03	3,124	1,590.9	+1.38	.14

<sup>1</sup> In all of these measurements the source of light was a helium tube, and they pertain to the yellow helium line ( $\lambda = 5876 \text{ \AA}$ ).

## V. CALCULATION BY CLAPEYRON EQUATION.

The Clapeyron equation combines the latent heat of vaporization  $L$ , the specific volumes of liquid  $u$ , and vapor  $u'$ , the slope of the vapor pressure-temperature curve  $\frac{dp}{d\theta}$ , and the temperature on the absolute scale  $\theta$ , as follows:

$$L = \theta (u' - u) \frac{dp}{d\theta}$$

<sup>29</sup> Jour. Amer. Chem. Soc., 41, p. 39; 1919.

All of these quantities except the one under discussion here have been determined for ammonia at this bureau with an accuracy of about 1 part in 1,000 within the interval  $-50$  to  $+50^{\circ}\text{C}$ . The calculation of the specific volume of the vapor from this equation is given in Table 8.

TABLE 8.—Specific Volume of Saturated Vapor Calculated from Clapeyron Equation.<sup>1</sup>

Temp.	$\theta$	$L$	$\frac{dp}{d\theta}$	$u$	$u'$
$^{\circ}\text{C}$ .	$^{\circ}\text{abs}$	Joules/g	mm Hg/ $^{\circ}\text{C}$ .	$\text{cm}^3/\text{g}$	$\text{cm}^3/\text{g}$
$-50\dots$	223.1	1,414.3	18.15	1.42	2,621.2
$-40\dots$	233.1	1,387.5	28.82	1.45	1,550.6
$-30\dots$	243.1	1,358.6	43.61	1.47	962.69
$-20\dots$	253.1	1,328.5	63.29	1.50	623.56
$-10\dots$	263.1	1,296.3	88.64	1.53	418.45
0...	273.1	1,262.4	120.35	1.57	289.66
10...	283.1	1,226.0	159.10	1.60	205.76
20...	293.1	1,187.1	205.50	1.64	149.47
30...	303.1	1,145.7	260.0	1.68	110.73
40...	313.1	1,100.5	323.3	1.73	83.28
50...	323.1	1,051.6	395.8	1.78	63.46

<sup>1</sup> These factors were reduced to consistent units by reducing  $L$  to ergs/g (1 Joule =  $10^7$  ergs) and  $\frac{dp}{d\theta}$  to dynes/cm<sup>2</sup>  $^{\circ}\text{C}$ . (1 mm Hg = 1,333.3 dynes/cm<sup>2</sup>).

In the above calculation the temperature of the ice point on the absolute thermodynamic scale has been taken as  $273.1^{\circ}$ , which is the value usually accepted as representing our present knowledge of that temperature. If it were possible to measure all of the above quantities with very high accuracy the Clapeyron equation would offer an excellent means of locating the ice point on the thermodynamic scale. These quantities for ammonia have been measured near that temperature with greater accuracy than for any other substance. It is interesting, therefore, although perhaps of no very great significance, to calculate this fundamental constant from the observed data now available.

For this calculation the individual measurements of the specific volume of the vapor by the direct method above  $20^{\circ}\text{C}$ . have been used.<sup>30</sup> The accuracy of the measurements at the lower temperatures is not sufficient to warrant giving them any considerable weight. The mean value obtained (see Table 9) is in fair agreement with the recent results of Hoxton<sup>31</sup> ( $273.36^{\circ}$ ) and of Henning and Heuse<sup>32</sup> ( $273.20^{\circ}$ ).

<sup>30</sup> In this calculation no correction has been applied for the superheat of the vapor. This correction if applied would increase the mean temperature of the ice point about  $0.05^{\circ}$ . Another correction should be applied for the film of liquid on the walls of the capillary above the free surface of the liquid (discussed in Section VII). The magnitude of this correction is difficult to estimate. Since these corrections are opposite in sign, they tend to compensate. In the opinion of the authors the correction for the film of liquid is at least as large as the correction for superheat and, therefore, the uncorrected value is probably nearer the truth.

<sup>31</sup> Phys. Rev., 13 (6), p. 438; 1919.

<sup>32</sup> Zeit. für Phys., 5, p. 285; 1921.



TABLE 9.—Calculation of the Thermodynamic Temperature of the Ice Point.<sup>1</sup>

Temp.	$u'$	$u$	$\frac{dp}{d\theta}$	$L$	Temperature calculated.	$\theta_0$	Picno-meter and series.
°C.	cm <sup>3</sup> /g	cm <sup>3</sup> /g	mm Hg/°C.	Joules/g	abs		
50.53	62.55	1.78	399.83	1,049.0	323.69	273.16	D(1)
46.32	69.98	1.76	368.00	1,070.2	319.72	273.40	D(2)
32.03	104.37	1.69	272.08	1,136.9	305.22	273.19	D(1)
25.07	128.09	1.66	232.08	1,166.5	298.17	273.10	E(3)
24.05	132.00	1.65	226.56	1,170.8	297.34	273.29	D(2)
23.53	134.11	1.65	223.78	1,173.0	296.80	273.27	E(1)
20.53	147.05	1.64	208.20	1,185.1	293.60	273.07	E(6)
20.37	147.71	1.64	207.30	1,185.9	293.74	273.37	E(2)
19.67	150.89	1.64	203.83	1,188.7	293.06	273.39	E(5)
Mean=						273.25	

## VI. FORM OF EMPIRICAL EQUATION EXPRESSING SPECIFIC VOLUME AS A FUNCTION OF TEMPERATURE.

For the computation of tables of the properties of a substance an empirical equation expressing one property as a function of another (usually the temperature) is a great convenience to the computer. It is also useful to obtain derivatives for thermodynamic calculations. Such an equation expressing the specific volume of the saturated vapor as a function of temperature has apparently not been proposed heretofore.

A form of empirical equation was sought which would represent the results closely and which would also satisfy the terminal conditions at the critical temperature. The equation should at that temperature give a finite value for the specific volume  $u'$  and approach the value  $-\infty$  for the derivative  $\frac{du'}{d\theta}$ . In view of the approximate reciprocal relationship between specific volume and vapor pressure, an equation similar to the vapor-pressure temperature equation suggested its possible usefulness with an additional term which would make it satisfy the second condition mentioned above. As in the case with vapor pressure no simple relation has been found which can be used even over a comparatively small interval of temperature.

An equation of the form

$$\log u' = A + \frac{B}{\theta} + C \log \theta + D\sqrt{\theta_c - \theta} + E(\theta_c - \theta)$$

where  $\theta_c$  is the critical temperature, was found to meet the above requirements.

<sup>1</sup> The values of the latent heat of vaporization here tabulated are expressed in absolute joules per gram. They were recomputed from the data given in the original paper (loc. cit.) using values of  $C_p$  which were recently determined at this bureau (published in *Refrig. Eng.* 9, p. 1: 1922) and the relation 1 International joule = 1.00034. Absolute joules as given in B. S. Circular No. 60, 2d ed.; 1920.

## VII. DISCUSSION OF RESULTS AND SOURCES OF ERROR.

A comparison of the results obtained by the two methods with those calculated from the Clapeyron equation is shown in Figure 4. It is evident that the results obtained by the two methods differ systematically in opposite directions and to practically the same extent from the Clapeyron values. It is of no little interest to consider the possible source of these systematic differences.

In the direct method significant errors in the determination of the apparent volumes of the liquid and vapor are quite improbable. They are more liable to be accidental than systematic. In the determination of the mass it is possible that some of the ammonia was absorbed on the surfaces of the picnometer during the course

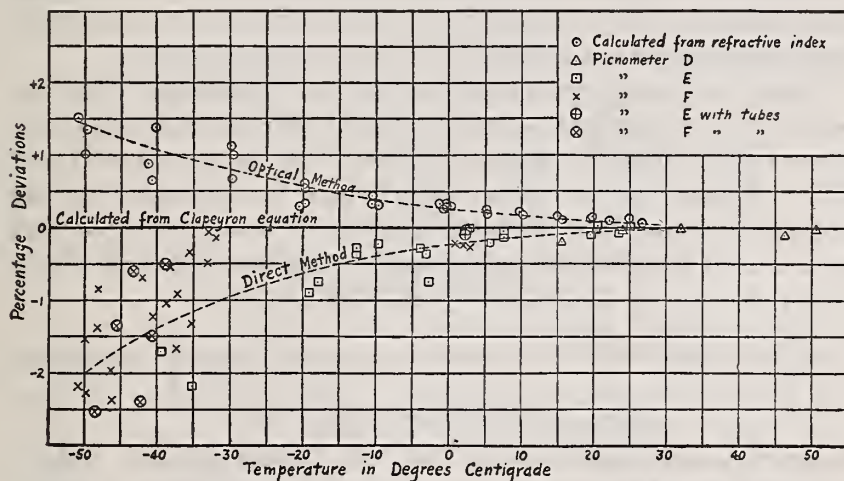


FIG. 4.—Comparison of experimental results obtained by both methods with values calculated from Clapeyron's equation.

of the experiments and was removed by evacuation before the final weighing of the picnometer, thus making the observed mass of ammonia vapor too large and the specific volume too small. The experiments with the increased surface area indicate, however, that this error is small and probably not greater than the accidental errors of measurement. A source of systematic error, the elimination of which is almost impossible in this method, although it might have been materially reduced, lies in the fact that the surface of the capillary between the bulb of the picnometer and the capillary containing the free surface of the liquid was undoubtedly wet with a film of liquid. The thickness of this film is difficult to estimate. Its effect is, of course, much greater at the low temperatures where the mass of the vapor is small and is in the direction of too small specific volumes.

In the optical method, aside from the accidental errors in the measurement of the fringe fractions, the vapor was necessarily superheated somewhat (probably less than a degree), which corresponds to high specific volumes. The amount of superheat was doubtless nearly the same in all cases, since condensation was observed to take place soon after each reading and would, therefore, affect all of the measurements to the same extent, namely, not more than about 0.3 per cent. A film of gas or liquid adsorbed on the interferometer plates and removed upon evacuation would, in effect, shorten the path difference of the light, and hence decrease the measured refractive index, making the calculated specific volumes too large. As shown in the last column of Table 7, the differences expressed in fractions of a fringe are of the order of one-tenth of a fringe which may possibly represent the approximate thickness of the adsorbed film, viz., 0.000003 cm.<sup>33</sup>

Since the Clapeyron values are in fair agreement with the results by both methods above 0° C. and differ from them at the lower temperatures by amounts (about 2 mg in one method and 0.1 of a fringe in the other), which may be attributed to the limitation of precision of those methods, it seems probable that they are not far from the true values. They are expressed within 1 part in 1,000 by the following empirical equation

$$\log_{10} u' = 300 \left[ \frac{6.46344}{\theta} - 0.106887 + 0.0356803 \log_{10} \theta \right] + 0.0862366 \\ \sqrt{406.1 - \theta} + 0.002667(406.1 - \theta)$$

where  $u'$  is expressed in cm<sup>3</sup>/g and  $\theta$  in degrees absolute (°abs = °C. + 273.1). The value for the critical temperature is based upon the experimental determination of Cardoso and Giltay.<sup>34</sup>

The above equation agrees at the critical temperature with the value found for the critical volume 4.28 cm<sup>3</sup>/g by extrapolation of the mean diameter of the temperature-density dome. The equation for the mean diameter which was found to agree closely with the observed data is

$$\frac{d_1 + d_2}{2} = 0.23355 + 6.956 \times 10^{-4} (133 - \theta) - 2.9 \times 10^{-7} (133 - \theta)^2$$

where  $d_1$  and  $d_2$  are the densities of the liquid and vapor, respectively, in gm/cm<sup>3</sup> and  $\theta$  is expressed in degrees centigrade.

A comparison of the values of the specific volume in the interval +50 to +100° C. obtained from various sources is shown in Table 10.

<sup>33</sup>  $\lambda = 5.876 \text{ \AA} = \text{approx. } 6 \times 10^{-5} \text{ cm}$ . Thus, one-tenth of a fringe is equivalent to a film  $3 \times 10^{-6} \text{ cm}$  thick on each plate or about 100 molecules in depth.

<sup>34</sup> Arch. Sci. Phys. Nat., Genève, 34, p. 20; 1912.



The second column represents values computed from the authors' equation. The third column was obtained by calculation from the Clapeyron equation, using the specific volumes of the liquid  $u$  and  $\frac{dp}{d\theta}$  measured at this bureau and values for the latent heat extrapolated by means of the equation given by Osborne and Van Dusen. The fourth column was calculated by using the above equation for the mean density, together with the measured liquid specific volumes. The fifth column represents values interpolated from the results given by Berthoud and the last column are values given by Dieterici.

TABLE 10.—Specific Volume of Saturated Vapor in  $\text{cm}^3/\text{g}$  in the Temperature Interval  $+50$  to  $+100^\circ \text{C}$ .

Temperature, degrees centigrade.	Calculated from—			Berthoud.	Dieterici.
	Authors' equation.	Clapeyron equation.	Mean density.		
60.....	48.81	48.83	49.02	48.4	48.6
70.....	37.78	37.87	38.21	37.8	37.8
80.....	29.34	29.47	29.82	30.1	30.2
90.....	22.75	22.94	23.28	23.7	24.4
100.....	17.52	17.75	18.01	18.1	19.2

### VIII. SUMMARY.

The specific volume of saturated ammonia vapor was measured in the temperature interval  $-50$  to  $+50^\circ \text{C}$ . by two methods—one involving a direct determination of the mass of the vapor contained in a known volume and the other, an optical method, involving measurements of the index of refraction of the vapor.

Three picnometers of different total volumes were used in the measurements by the direct method. The effect of adsorption was studied and found to be of a magnitude comparable with the limit of accuracy of that method.

A Fizeau-Pulfrich interferometer was used in the measurements of the refractive index, and the Gladstone and Dale relation,  $u'(n-1) = \text{constant}$ , was assumed to be correct within 1 part in 1,000. The validity of this assumption for pressures here dealt with is well borne out by experiment.

Values for the specific volume were calculated from the Clapeyron equation, using other data obtained at this bureau. The experimental results found by the two methods are in fair agreement with the calculated values above  $0^\circ \text{C}$ ., differing at most by about 0.3 per cent. Below  $0^\circ \text{C}$ . the results found by the direct method are systematically lower and those found by the optical

method are systematically higher than the Clapeyron values, amounting to about 2 per cent at  $-50^{\circ}\text{C}$ . The calculated values were chosen, therefore, as the most probable values. The possible sources of error in the two methods are discussed. The final results are represented closely by the empirical equation:

$$\log_{10} u' = 300 \left[ \frac{6.46344}{\theta} - 0.106887 + 0.0356803 \log_{10} \theta \right] + 0.0862366 \sqrt{406.1 - \theta} + 0.002667 (406.1 - \theta)$$

in which  $u'$  is expressed in  $\text{cm}^3/\text{g}$  and  $\theta$  in degrees absolute ( $^{\circ}\text{abs} = ^{\circ}\text{C} + 273.1$ ).

In conclusion, the authors wish to acknowledge their indebtedness to the late Dr. C. W. Waidner for constant advice during this investigation; also to Dr. D. R. Harper, 3d, who was associated with the problem in its early stages; to C. S. Taylor, who assisted in the preparation of the pure ammonia; and to C. G. Peters for his hearty cooperation and valuable assistance in the measurements of the refractive index.

## APPENDIXES.

### APPENDIX 1.—Specific Volume of Saturated Ammonia Vapor.

#### CUBIC CENTIMETERS PER GRAM.

Temperature.	0	1	2	3	4	5	6	7	8	9
$-40^{\circ}\text{C} \dots$	1,551.0	1,631.0	1,716.0	1,806.0	1,901.0	2,002.0	2,111.0	2,226.0	2,350.0	2,482.0
$-30^{\circ}\text{C} \dots$	962.5	1,008.0	1,056.0	1,106.0	1,160.0	1,215.0	1,274.0	1,336.0	1,403.0	1,475.0
$-20^{\circ}\text{C} \dots$	623.5	650.0	678.0	707.5	738.5	771.5	806.0	841.5	879.5	920.0
$-10^{\circ}\text{C} \dots$	418.5	435.0	452.0	470.0	489.0	508.5	529.5	551.5	574.5	598.5
$0^{\circ}\text{C} \dots$	289.7	300.1	311.0	322.5	334.4	346.9	360.0	373.6	387.9	402.8
$0^{\circ}\text{C} \dots$	289.7	279.7	270.0	260.8	251.9	243.4	235.2	227.4	219.9	212.7
$+10^{\circ}\text{C} \dots$	205.8	199.1	192.7	186.6	180.7	175.0	169.5	164.2	159.1	154.2
$+20^{\circ}\text{C} \dots$	149.45	144.95	140.55	136.35	132.25	128.35	124.55	120.95	117.40	114.00
$+30^{\circ}\text{C} \dots$	110.75	107.55	104.45	101.50	98.65	95.85	93.20	90.60	88.05	85.65
$+40^{\circ}\text{C} \dots$	83.28	81.02	78.82	76.68	74.61	72.61	70.66	68.77	66.94	65.17

#### CUBIC FEET PER POUND.

$-40^{\circ}\text{F} \dots$	24.84	25.54	26.27	27.02	27.79	28.59	29.42	30.28	31.16	32.08
$-30^{\circ}\text{F} \dots$	18.96	19.46	19.99	20.53	21.09	21.66	22.25	22.87	23.50	24.16
$-20^{\circ}\text{F} \dots$	14.67	15.04	15.42	15.81	16.22	16.64	17.08	17.52	17.99	18.46
$-10^{\circ}\text{F} \dots$	11.50	11.78	12.06	12.36	12.66	12.97	13.29	13.62	13.96	14.31
$0^{\circ}\text{F} \dots$	9.114	9.32	9.54	9.76	9.99	10.22	10.46	10.71	10.97	11.23
$0^{\circ}\text{F} \dots$	9.114	8.911	8.712	8.520	8.332	8.149	7.971	7.797	7.628	7.464
$+10^{\circ}\text{F} \dots$	7.304	7.148	6.996	6.847	6.703	6.562	6.425	6.291	6.161	6.034
$+20^{\circ}\text{F} \dots$	5.910	5.789	5.672	5.557	5.445	5.336	5.230	5.126	5.024	4.925
$+30^{\circ}\text{F} \dots$	4.827	4.733	4.640	4.550	4.462	4.375	4.291	4.209	4.129	4.050
$+40^{\circ}\text{F} \dots$	3.974	3.899	3.826	3.754	3.684	3.616	3.549	3.484	3.420	3.357
$+50^{\circ}\text{F} \dots$	3.296	3.236	3.178	3.121	3.065	3.010	2.957	2.904	2.853	2.803
$+60^{\circ}\text{F} \dots$	2.754	2.706	2.658	2.612	2.567	2.522	2.479	2.436	2.394	2.354
$+70^{\circ}\text{F} \dots$	2.314	2.275	2.236	2.199	2.162	2.126	2.091	2.056	2.022	1.989
$+80^{\circ}\text{F} \dots$	1.956	1.924	1.893	1.862	1.832	1.803	1.774	1.745	1.717	1.690
$+90^{\circ}\text{F} \dots$	1.663	1.637	1.611	1.585	1.560	1.536	1.511	1.488	1.464	1.442
$+100^{\circ}\text{F} \dots$	1.419	1.398	1.376	1.355	1.334	1.314	1.294	1.274	1.255	1.236
$+100^{\circ}\text{F} \dots$	1.217	1.199	1.181	1.163	1.146	1.129	1.112	1.095	1.079	1.063
$+120^{\circ}\text{F} \dots$	1.048	1.032	1.016	1.001	.986	.970	.955	.940	.925	.910

## APPENDIX 2.—Density of Saturated Ammonia Vapor.

## GRAMS PER LITER.

Tempera- ture.	0	1	2	3	4	5	6	7	8	9
-40° C....	0.645	0.613	0.583	0.554	0.526	0.500	0.474	0.449	0.426	0.403
-30° C....	1.038	.992	.947	.904	.863	.823	.785	.748	.713	.678
-20° C....	1.604	1.538	1.475	1.413	1.354	1.296	1.241	1.188	1.137	1.087
-10° C....	2.390	2.299	2.212	2.128	2.046	1.967	1.889	1.813	1.741	1.671
0° C....	3.452	3.332	3.215	3.101	2.990	2.883	2.778	2.677	2.578	2.483
0° C....	3.452	3.575	3.702	3.834	3.970	4.109	4.252	4.398	4.548	4.702
+10° C....	4.860	5.023	5.189	5.359	5.534	5.714	5.900	6.090	6.285	6.485
+20° C....	6.690	6.900	7.115	7.335	7.560	7.791	8.028	8.270	8.518	8.771
+30° C....	9.030	9.295	9.570	9.850	10.140	10.435	10.735	11.040	11.355	11.680
+40° C....	12.010	12.345	12.690	13.040	13.400	13.770	14.150	14.540	14.940	15.345

## POUNDS PER CUBIC FOOT.

-40° F...	0.04026	0.03915	0.03807	0.03701	0.03598	0.03498	0.03399	0.03303	0.03209	0.03117
-30° F...	.05275	.05138	.05004	.04874	.04746	.04621	.04498	.04377	.04259	.04142
-20° F...	.06819	.06650	.06485	.06322	.06163	.06007	.05854	.05704	.05558	.05415
-10° F...	.08696	.08491	.08290	.08093	.07900	.07711	.07525	.07343	.07165	.06990
0° F...	.10970	.10725	.10483	.10245	.10011	.09782	.09556	.09335	.09113	.08905
0° F...	.10970	.11225	.11480	.11740	.12000	.12270	.12545	.12825	.13110	.13400
+10° F...	.13690	.13990	.14295	.14605	.14920	.15240	.15565	.15895	.16230	.16575
+20° F...	.16920	.17275	.17630	.17995	.18365	.18740	.19120	.19510	.19905	.20305
+30° F...	.20715	.21130	.21550	.21980	.22415	.22855	.23305	.23760	.24220	.24690
+40° F...	.25165	.25650	.26140	.26640	.27145	.27655	.28180	.28705	.29240	.29785
+50° F...	.3034	.3090	.3147	.3204	.3263	.3322	.3382	.3443	.3505	.3568
+60° F...	.3631	.3696	.3762	.3828	.3896	.3965	.4034	.4105	.4177	.4249
+70° F...	.4322	.4397	.4472	.4548	.4626	.4704	.4783	.4864	.4946	.5028
+80° F...	.5112	.5198	.5283	.5370	.5458	.5547	.5638	.5730	.5823	.5918
+90° F...	.6014	.6111	.6209	.6309	.6410	.6512	.6616	.6722	.6829	.6936
+100° F...	.7045	.7156	.7267	.7381	.7496	.7612	.7730	.7849	.7971	.8094
+110° F...	.8218	.8342	.8470	.8598	.8728	.8861	.8995	.9131	.9268	.9406
+120° F...	.9546	.9690	.9838	.9990	1.0146	1.0306	1.0470	1.0638	1.0810	1.0986



APPENDIX 3.—Specific Volume of Saturated Ammonia Vapor in Cubic Feet per Pound as Computed by Various Writers and Given in Their Ammonia Tables.

Temperature.		Ledoux, 1878.	Peabody, 1889.	Wood, 1889.	Zeuner, 1890.	Mollier, 1895.	Dieterich, 1904.	Wobsa, 1908.
° F.	° C.							
—49	—45							
—40	—40	25.07	26.10	24.37	25.63	25.66		
—31	—35	19.72	20.30	19.20	20.13	20.14		
—22	—30	15.66	16.00	15.24	15.96	15.99		15.80
—13	—25	12.55	12.70	12.22	12.76	12.81		12.59
—4	—20	10.16	10.25	9.87	10.31	10.35		10.13
+5	—15	8.29	8.31	8.07	8.39	8.41		8.23
+14	—10	6.82	6.83	6.63	6.89	6.92		6.74
+23	—5	5.64	5.65	5.49	5.70	5.73		5.56
+32	0	4.73	4.74	4.58	4.75	4.77	4.709	4.634
+41	5	3.98	3.99	3.84	3.99	4.00	3.932	3.884
50	10	3.38	3.38	3.24	3.37	3.38	3.300	3.274
59	15	2.89	2.89	2.75	2.87	2.88	2.787	2.776
68	20	2.48	2.48	2.35	2.46	2.47	2.371	2.366
77	25	2.15	2.15	2.02	2.12	2.11	2.026	2.026
86	30	1.87	1.87	1.74	1.84	1.83	1.738	1.744
95	35	1.64	1.63	1.51	1.61	1.59	1.493	1.509
104	40	1.45	1.44	1.315	1.41	1.39	1.296	1.309
113	45			1.152			1.136	
122	50			1.014			0.998	
140	60			0.791			0.778	
158	70			0.628			0.605	
176	80						0.484	
194	90						0.391	
212	100						0.308	

Temperature.		Hütte Macintire, 1911.	Hybl, 1911.	Lucke, 1912.	Good- enough and Mosher, 1913.	Holst, 1915.	Keyes and Brown- lee, 1916.	Bureau of Stand- ards, 1923.
° F.	° C.							
—49	—45				32.98		32.87	32.12
—40	—40			25.72	25.45	25.03	25.36	24.86
—31	—35			19.84	19.87	19.65	19.79	19.48
—22	—30	15.79	15.80	15.70	15.68	15.59	15.62	15.43
—13	—25	12.65	12.55	12.50	12.51	12.50	12.48	12.36
—4	—20	10.21	10.11	10.12	10.08	10.11	10.06	9.991
+5	—15	8.30	8.23	8.22	8.20	8.25	8.20	8.150
+14	—10	6.80	6.76	6.75	6.72	6.79	6.73	6.703
+23	—5	5.61	5.59	5.54	5.560	5.626	5.576	5.556
+32	0	4.668	4.635	4.66	4.631	4.695	4.650	4.637
+41	5	3.907	3.900	3.91	3.884	3.944	3.904	3.897
50	10	3.285	3.287	3.32	3.278	3.332	3.298	3.294
59	15	2.779	2.784	2.80	2.783	2.832	2.802	2.800
68	20	2.369	2.369	2.40	2.377	2.419	2.393	2.393
77	25	2.026	2.026	2.05	2.039	2.076	2.052	2.055
86	30	1.741	1.743	1.76	1.759	1.789	1.770	1.772
95	35	1.504	1.507	1.52	1.524	1.547	1.532	1.534
104	40	1.304	1.307	1.32	1.325	1.344	1.330	1.334
113	45			1.14	1.156		1.158	1.163
122	50			1.000	1.012		1.011	1.017
140	60			0.770	0.784		0.777	
158	70			0.600	0.613		0.601	
176	80			0.464	0.483		0.469	
194	90			0.364	0.381		0.361	
212	100				0.301			

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